"Trends in Great Lakes Fish Contaminants"

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For Data and Trend Analysis of 1999 and 2000 Fish

By

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I. INTRODUCTION AND BACKGROUND

This report provides the data and trend analysis for the years 1999 and 2000 for the Great Lakes Fish Monitoring Program (GLFMP), a cooperative program of the US EPA Great Lakes National Program Office (GLNPO) and the USGS Biological Research Division (BRD).

This project addresses two programmatic components of the GLFMP: Element 1 determines the contaminant concentrations in 600-700 mm lake trout (*Salvelinus namaycush*) whole fish composites (5 fish) from each of the lakes (walleye, *Stizostedion vitreum vitreum*, in Lake Erie). These data are used to assess time trends in organic contaminants in the open waters of the Great Lakes, using fish as biomonitors. These data can also be used to assess the risks of such contaminants on the health of this important fishery, and on wildlife that consume them. Element 2 focuses on assessing human exposures via consumption of popular sport fish. Coho (*Oncorhynchus kisutch*) and chinook salmon (*Oncorhynchus tshawytscha*) from each lake (rainbow trout, *Salmo gairdneri*, in Lake Erie) are collected during the fall spawning run, and composite fillets (5 fish) are analyzed for organic contaminants to assess human exposure. These data also complement those from Element 1. The coho salmon spawn at 3 years of age, and so their body burdens reflect a more focused and consistent exposure time compared to the lake trout which may integrate exposures over 4 to 10 yrs, depending on the lake. Chinook salmon spawn after 4-5 years, and have higher (and thus more detectable) concentrations than the coho salmon and also represent a consistent exposure time. Thus time trends for consistent age fish as well as consistent size fish can be assessed from these data where sufficient data exist.

Fish monitoring programs of various size efforts have been conducted in the Great Lakes since the 1970's by a number of state, provincial, and federal agencies, but did not have consistent methodologies or aims. The GLFMP was implemented as a coordinated effort that consisted of a Cooperative Agreement between EPA GLNPO and the US Fish & Wildlife Service (the office involved is now the National Biological Division of the US Geological Survey) and the Great Lakes states. The Department of Fisheries and Oceans of Canada has also monitored organic contaminants in fish since the late 1970s (De Vault et al. 1995). The goals of the GLFMP are to monitor time trends in bioaccumulative organic chemicals in the Great Lakes using top predator fish as biomonitors, and to assess human exposure to organic contaminants

found in fall run coho and chinook salmon. The program design is to meet the primary data quality objective to detect contaminant change of 25% with 95% confidence.

This highly visible and successful program has provided the Great Lakes community with one of the most useful long-term data sets of organic contaminants on record. No comparable data sets for contaminant concentrations in water exist, and sediment core records of organic contaminants are not available for all compounds of concern in all the lakes. Numerous reports and publications of the interpretation of these data resulted from EPA scientists involved in the GLFMP (De Vault and Weishaar 1983; De Vault 1984; De Vault and Weishaar 1984; De Vault 1985; De Vault et al. 1985; De Vault et al. 1986; De Vault et al. 1988; De Vault et al. 1996), many of which are highly cited. These publications have shown that the concentrations of chemicals that have been banned or whose sources are controlled have declined in a first-order exponential pattern. The classic examples are the trends in PCBs and ΣDDT, both of which were banned in the 1970s. In addition, these data have been used to demonstrate that PCBs have stopped declining in Lake Michigan (Stow et al. 1995; De Vault et al. 1996), not because of new sources but because of changes in the foodweb (De Vault et al. 1996; Madenjian et al. 1998; Madenjian et al. 1999). Other contaminants show different time trends. Toxaphene has shown no decline in Lake Superior fishes but appears to have declined in the other lakes (Glassmeyer et al. 1997).

These data have also served as a valuable resource for other scientists who have used them to corroborate trends from other media such as water and sediment (Rodgers and Swain 1983; Jeremiason et al. 1994; Pearson et al. 1996), to construct or calibrate models of contaminant bioaccumulation (Stow et al. 1994; Stow and Carpenter 1994; Stow 1995; Stow et al. 1995; Jackson and Schindler 1996; Eby et al. 1997; Stow and Qian 1998), or to assess the health of the fishery (Mac and Edsal 1991; Mac et al. 1993; Cook et al. 1997, 2003).

II. METHODS

Fish Samples. All fish samples were supplied by USGS BRD as frozen homogenates. The lake trout composites consist of 5 whole fish between 600-700 mm and the walleye composites consist of 5 whole fish between 450-550 mm. The fall run coho and chinook salmon composites consist of 5 skin-on fillets. Coho salmon stocking is declining in Lake Erie, and thus rainbow trout are substituted as a monitoring species. Rainbow trout composites consist of 5 skin-on

fillets. The records of length, weight, and sex of each fish in the composite were provided by USGS BRD. A summary of the composites that were received is shown in Tables 1 and 2.

Table 1. Fish collections and composite characteristics for Element 1. "N" signifies the number of composites.

Lake	Year	Fish species	# N	Site
Superior	1999	lake trout	10	Keweenaw Pt.
	2000	lake trout	10	Apostle Islands
Huron	1999	lake trout	10	Port Austin
	2000	lake trout	10	Rockport
Michigan	1999	lake trout	9	Sturgeon Bay
	2000	lake trout	10	Saugatuck
Erie	1999	walleye	7	Dunkirk
	2000	walleye	6	Middle Bass Isl.
Ontario	1999	lake trout	10	N. Hamlin
	2000	lake trout	10	Oswego

*coho are no longer being stocked in L. Erie and thus rainbow trout are the preferred monitoring species.

Ideally, 10 lake trout composites are obtained from each lake for the sampling site for that year. In 1999, only 9 lake trout composites were collected from Sturgeon Bay, Lake Michigan, and 7 walleye composites from Dunkirk, Lake Erie. The other lakes had 10 composites. In 2000, 10 composites were received from each lake except for Lake Erie, where only 6 composites of walleye were collected.

Table 2. Fish collections and composite characteristics for Element 2. "N" signifies the number of composites.

Lake	Year	Fish Species	# N	Sites
Superior	1999	Chinook	3 each site = 6	Pikes' Creek (Sioux River), French River
	2000	coho	3 each site = 0	
Huron	1999	Chinook	3 each site = 6	Swan River, Ausable Pt (Tawas River)
	2000	Chinook	3 one site = 3	Swan River
Michigan	1999	Chinook	3 each site = 18	Trail Cr., Grand R., St. Joseph R., Thompson Cr. Hatchery, Root R., Platte R.
	2000	coho	3 each site = 12	Kewaunee, Trail Creek, Thompson River, Grand
Erie	1999	Steelhead	3 each site = 6	Trout Run, Grand River
	2000	Steelhead	3 one site = 3	Trout Run
Ontario	1999	Chinook	3 each site = 3	Salmon River
	2000	coho	3 each site = 0	

Note that Steelhead trout were collected in Lake Erie instead of either Chinook or coho salmon, and that the anticipated number of composites was not always realized due to collection problems.

Sample Extraction and Interference Removal for Organic Compounds. Samples are thawed and homogenized. A 2 g subsample (exact weight recorded) is mixed with approximately 14 g anyhdrous sodium sulfate to obtain a mealy texture. The mixture is transferred quantitatively to a Soxhlet extractor charged with 150 mL of methanol (MeOH) in a 250 mL roundbottom flask. A set of samples consists of four fish samples, one QA sample (duplicate, spike sample, etc.) and a procedural blank. A procedural blank consists of sodium sulfate without fish carried through the procedure in a manner identical to the samples. An aliquot of surrogate recovery standard solution is added by micropipette. The sample is extracted for 4 hours. The MeOH is removed to a separatory funnel, and the Soxhlet charged with 150 mL dichloromethane (DCM). The sample is extracted for an additional 18 hrs. The MeOH is extracted by adding 75 mL sodium chloride-saturated organic free water and back-extracting three times with hexane (3 x 25 mL). This extract is dried with anhydrous sodium sulfate and combined with the second Soxhlet extract, transferred to a Kuderna-Danish (KD) apparatus with Snyder column and reduced in volume and solvent-exchanged to hexane using a steam bath. The extract is brought to exactly 10 mL in hexane, and exactly 1 mL is removed for lipid analysis (see below).

Lipids and other organic compounds must be removed from the extract to accurately detect and quantify the analytes of interest. Lipids are removed by a column (1 x 30 cm) containing 13 g 6% deactivated alumina (60 mesh, w/w) and eluting with 3 x 30 mL hexane. The eluate is collected in a KD and reduced in volume as before to approximately 10 mL. This extract is then placed on a column containing 4.5 g fully activated silica gel over 6 g 1% deactivated neutral alumina (w/w), with anhydrous sodium sulfate above and below each layer. The column is eluted with 3 x 30 mL hexane (Fraction 1). The column is further eluted with 3 x 30 mL 40%/60% DCM/hexane (Fraction 2). Each fraction is solvent exchanged to hexane and reduced to a volume of approximately 1 mL. At this time the extract is stored in a vial with teflon-lined cap and stored in a freezer. Prior to instrumental analysis, the extract is reduced to a few hundred microliters by gentle nitrogen gas stream, and the internal standard is added (PCB #204) to Fraction 1. A separate extraction of fish is required for Hg (see below).

Extract Instrumental Analysis. For the 1999 fish, four separate analyses were done on a given extract to quantitate all the required organic analytes: (1) PCB congeners; (2) PCB coplanar congeners; (3) toxaphene, chlordanes, and nonachlors; and (4) organochlorine pesticides. Following the recommendations of the Emerging Contaminants Workshop participants (see below), additional analytes were added, which increased the number of analysis groups to six. PBDEs, and PBB-153 were added, and included in the OC analysis group, and PCDD/Fs and PCNs were added as two additional analysis groups. Mercury was also added to the analyte list, and it requires a separate extraction and analysis. The analysis for PCBs is done first on Fraction 1. Once the data have been reviewed and found to be acceptable, then Fraction 1 and 2 are recombined (hence no need for an internal standard in Fraction 2) and the 3rd through 6th analyses are done on the combined extract. This is because of the high potential of interference from other compounds in PCB analyses. The other compounds do not experience interference from the PCBs and our experience has been that recoveries are improved if the two fractions are recombined. Full details of the analytical methods can be found in the approved QAPP for this project.

PCB congeners are analyzed by gas chromatography with electron capture detection (GC-ECD). The method resolves and quantifies 110 congener or congener groups, and is similar to that used for the GLNPO Lake Michigan Mass Balance Study (Swackhamer and Trowbridge 1997) and previous Great Lakes PCB studies (Pearson et al. 1996; Skoglund et al. 1996; Swackhamer 1996). The GC (Hewlett Packard 5988) is equipped with an autosampler, large volume splitless injector, 60 m DB-5 column, Ni-63 ECD, and HP ChemStation data acquisition software. The injection port is kept at 225 ^{o}C, the oven is programmed from 100 ^{o}C to 280 ^{o}C at 1 deg/minute, and the detector is maintained at 325 ^{o}C. The carrier gas is hydrogen and the makeup gas is argon-in-methane.

The above method does not separate all of the toxic co-planar congeners, which preferentially bioaccumulate in fish relative to other PCBs (Trowbridge and Swackhamer 1999) and may be of interest particularly to the Great Lakes states health authorities because of their human health significance (Safe 1994). We use another analysis for the co-planar congeners (Trowbridge and Swackhamer 1999), which is a modification of a method developed by Schmidt and Hesselberg (1992) and uses gas chromatography mass spectrometry (GCMS) in electron capture negative ion mode (ECNI). This method utilizes the fact that GC/MS in the negative ion

mode is very selective and sensitive to highly chlorinated compounds. AHH-inducing PCB congeners often co-elute with other congeners having a different number of chlorine atoms, which allows them to be differentiated by GCMS-ECNI. The GC separation is the same, using helium as the carrier gas. The MS (Hewlett Packard 5988) has ChemStation and Aquarius acquisition software. The transfer line is maintained at 270 °C, the source temperature and pressure is 100 °C and 1 torr, the reagent gas is methane.

Toxaphene, chlordanes and nonachlors and all other organochlorines are analyzed by GCMS-ECNI. This technique is as sensitive as GC-ECD, but is far more accurate because it affords a means of eliminating interferences and providing confirmation from the resulting mass spectra. One injection and temperature program is used for the toxaphene, chlordanes, nonachlors, and a second injection and program is used to acquire the data for the remaining organochlorine compounds.

Toxaphene is a complex mixture of hundreds of compounds, and thus requires a separate analysis. Because of the similarities in mass spectra, cis- and trans-chlordane, and cis- and trans-nonachlor are also analyzed in the same run. The method quantitates total toxaphene, and the contributions of each of its homologs (hexa-, hepta-, octa-, nona-, and deca-chlorinated bornanes and bornenes), and was originally developed by this investigator (Swackhamer et al. 1987) and subsequently modified by Glassmeyer (1999). We now use a modification of this method (Swackhamer, unpublished) that includes strict confirmation criteria to exclude non-toxaphene interferences. The method monitors selected ions for each of the bornane and bornene homologs, as well as for known interferences so that they can be accounted for. Quantitation and confirmation ions for the chlordane and nonachlor components are also included. All GCMS conditions are similar to those described above, but a slightly different temperature program is used to optimize baseline resolution of the different compounds.

All other chlorinated compounds (see Table 3) are analyzed by GCMS-ECNI by monitoring selected ions for quantifying and confirming each compound. All GCMS conditions are as described above, but a slightly different temperature program is used to optimize resolution.

The fraction lipid of each sample is determined gravimetrically by weighing exactly 1/10 of the extract of a known mass of fish tissue and taking to complete dryness and reweighing to constant weight.

Data Processing and Quantification Methods. All chromatograms are carefully reviewed by an experienced operator. The ChemStation software automatically integrates all peaks of interest, and to ensure accurate integration, the baselines are also reviewed by an experienced operator for integrity. We use a Basic program to check the quantification and confirmational ion area ratios for QA purposes and to eliminate false positives. The peak areas are transferred electronically to a PC spreadsheet template that uses the internal standard method to quantitate the mass of analyte in each extract. The equation used is as follows:

$$Mass_{analyte} = area_{analyte} * mass_{IS}/area_{IS} * RRF$$

Where $RRF = (mass_{qstd}/area_{qstd})/(mass_{IS}/area_{IS})$
                 IS = internal standard
                 $qstd$ = quantification standard

The spreadsheet formulas are checked regularly for accuracy using check standards. The mass of analyte in each extract is converted to a concentration by dividing by the exact mass of fish tissue that was extracted. Concentrations are reported as mass analyte per gram of fish, wet weight basis (typically ng/g).

Summary Statistics. Arithmatic means and 95% confidence limits are computed for the lake trout for each lake and each year. Samples of the same species from the same lake and year are field replicates. In general, values with a QA qualifier are not included; however, all data and statistics are reviewed by the PI. Professional judgment is used to determine which values if any are not included in the summary statistics. Values below the MDL are not included, unless inclusion of them would not affect the mean significantly. For those samples that have an unacceptable surrogate recovery, the analyte data associated with that surrogate is reviewed and if it is consistent with (within the 95% confidence limit) of the mean, it is still included in the summary statistics. Conversely, if a sample meets QA criteria, but an analyte value is outside of the 95% confidence limit, it is considered an outlier and excluded from the summary statistics.

Table 3. List of organic chemicals analyzed in fish, their surrogate recovery standards, type of instrumental analysis used, approximate MDL expressed as pg/g wet fish tissue, and the m/z used in quantification (Q) and confirmation (C) for MS analyses.

Analyte	Surrogate	analysis[‡]	MDL, ng/g	Q, C m/z
PCB congeners	PCB- 65, 188	GC-ECD	1 - 10	N/A
PCB co-planars	PCB-65, 188	GCMS-ECNI 1	1 - 10	By homolog
hexachlorobenzene	^{13}C-hexachlorobenzene	GCMS-ECNI 2	1	284/286
Pentachlorobenzene	^{13}C-hexachlorobenzene	GCMS-ECNI 2	5	250/252
Octachlorostyrene	^{13}C-hexachlorobenzene	GCMS-ECNI 2	0.5	380/378
δ-BHC (Lindane)	^{13}C-BHC	GCMS-ECNI 2	1	255/257
α-BHC	^{13}C-BHC	GCMS-ECNI 2	1	255/257
Aldrin	^{13}C-chlordane	GCMS-ECNI 2	5	330/332
Dieldrin	^{13}C-chlordane	GCMS-ECNI 2	5	380/346
Heptachlor epoxide a	^{13}C-chlordane	GCMS-ECNI 2	5	237/239
Heptachlor epoxide b	^{13}C-chlordane	GCMS-ECNI 2	5	237/239
Cis-chlordane	^{13}C-chlordane	GCMS-ECNI 3	0.5	406/408
Trans-chlordane	^{13}C-chlordane	GCMS-ECNI 3	0.5	406/408
Cis-nonachlor	^{13}C-chlordane	GCMS-ECNI 3	0.5	444/442
Trans-nonachlor	^{13}C-chlordane	GCMS-ECNI 3	0.5	444/442
Oxychlordane	^{13}C-chlordane	GCMS-ECNI 2	1	424/422
pp, op-DDT	^{13}C-p,p-DDE	GCMS-ECNI 2	1	281/283; 248/246
pp, op-DDE	^{13}C-p,p-DDE	GCMS-ECNI 2	1	281/283; 246/248
pp, op-DDD	^{13}C-p,p-DDE	GCMS-ECNI 2	1	248/250; 248/246
Endrin	^{13}C-chlordane	GCMS-ECNI 2	5	380/346
Mirex	^{13}C chlordane	GCMS-ECNI 2	1	404/402
Toxaphene&homologs	^{13}C chlordane	GCMS-ECNI 3	10 (total)	Homologs[%]
PCDD/Fs	^{13}C PCDD/Fs	GCMS-ECNI 4	10	Homologs[%]
PBDEs	PBDE-71, -188, -166	GCMS-ECNI 5	0.3 (congeners)	79/81
PCNs	^{13}C PCNs	GCMS-ECNI 5	1-10 (congeners)	Homologs[%]
Dacthal	^{13}C-p,p-DDE	GCMS-ECNI 2	10	332/330
PBB-153	PBDE-71, -188, -166	GCMS-ECNI 5	0.3	79/81
Hg	N/A	CVAFS	10	N/A
Fraction lipid	N/A	gravimetrically	0.05%	N/A

* Additional surrogates are available if desired; surrogates chosen to represent groups of compounds based on structure.

** Analyte added for 2000 analyes.

[‡] GCMS-ECNI 1-5 refer to five different MS analyses of the same extract.

III. QUALITY ASSURANCE

A. QAPP Preparation and Approval

A Quality Assurance Project Plan (QAPP) was developed and submitted to GLNPO for review and approval. After a series of drafts that reflected comments from GLNPO, and that reflected the changes in our workplan regarding the Workshop on Emerging Contaminants (see below) and the change in analyte list, a final QAPP (v.6) was approved in September 2002. A revised QAPP (v.7) was submitted and approved in July 2004 that reflected changes in the program. This also reflects the considerable effort that went into validating the new analyte methods, and evaluating the quality assurance (QA) components for the overall GLFMP. To my knowledge, a thorough review of the QA components was not done by BRD after the departure of Dr. Robert Hesselberg (1996). QAPP v.7 also reflects revisions resulting from the Laboratory QA Site Visit in March, 2003.

B. Laboratory QA Site Visit by GLNPO

A team from EPA GLNPO visited the Environmental Chemistry Laboratory on March 6-7, 2003. This team consisted of Mr. Louis Blume, GLNPO QA Officer; Mr. George Schupp, Deputy Director of CRL; Dr. Wayne Whipple, organic chemist from CRL; and Dr. Harry McCarty, senior scientist at Dyne Corp. A written report of the visit was provided to Dr. Swackhamer. The overall assessment of the lab based on this site visit was "quite positive". She was commended for training and supervising her personnel well, and for providing well maintained facilities for the project. A series of 8 recommendations were made to improve the program, and responses to those recommendations are detailed below. In general, all of the suggestions have been incorporated.

1) The QAPP has been amended to expand on staff training to include (a) documentation of the existing practice of requiring new staff to demonstrate their lab capabilities by preparing and analyzing a set of spiked fish (initial demonstration of competence, or IDC). (b) a revision of the Data Completeness discussion to define completeness as a goal, not a requirement, and to lower the criteria from 95% to 90%. (c) the removal of

all discussion of field duplicates and acceptance criteria, as there are no true field duplicates in the sample collection program.

2) The SOPs have been modified to include (a) the list of analytes included in a given analysis as well as the concentration ranges over which the lab is confident for quantifying samples and actions taken if these ranges are exceeded; (b) a duplication of the QA criteria and control actions from the QAPP; (c) documentation of how lab activities are documented; (d) page numbers and date of SOP to avoid confusion among revisions.

3) We have incorporated a monitoring protocol for DDT and endrin degradation in the injection port, with a control limit of 15% degradation allowed.

4) We acknowledge that the HP 5988 GCMS is a stumbling block to efficient progress on the grant, and are testing out a state-of-the-art 5973 GCMS for future purchase.

5) Dr. Nater has conducted a series of studies that have determined that the minimum sample size of fish needed to meet precision requirements is 1 gram rather than 0.2 grams.

6) Dr. Nater has developed an improved method to reduce the coating of his instrument parts by lipid during analyses.

7) We have developed a QA summary sheet for tracking aggregate QA data.

8) We have purchased and installed battery-operated thermometers for all freezers used by the project.

C. QA Results

Check Samples. Early in the implementation of the GLFMP (1980s), a large composite of lake trout from Sturgeon Bay, Lake Michigan was prepared by Dr. Robert Hesselberg of the then USFWS and 10 g subsamples were distributed among glass jars and frozen. These were to serve a check samples to track reproducibility and comparability within a lab and between labs. This check sample was used up sometime in the mid-1990s, and a new sample was prepared by USGS-BRD. We do not have the data that compares this newer check sample with the old check sample, but we have some of the BRD data on the new check sample with which to compare our data. It should be noted, however, that instead of freezing discreet samples to be analyzed periodically, a single large "brick" of fish was sent to us and thus the entire sample had to be

thawed and refrozen. The impact of this sample treatment on comparability to the BRD lab is unknown. Future check samples should be prepared using the original protocol.

The results of our check sample analyses are shown below, along with a comparison of our data to BRD. We achieved the QA goal of reproducibility (30% CV) with an n=8, with the exception of t-chlordane. All of our data are surrogate corrected. Our data are reasonably comparable to the BRD data (the number of analyses used to obtain these means was not provided). Four of the analytes did not meet QA at BRD, including c-nonachlor, pentachlorophenol, OCS, and endrin. None of these is an important contaminant when viewing the current field data. Our overall reproducibility within our lab was 13% ± 11%; the overall reproducibility within BRD was 28% ± 11%. The mean relative percent difference between our two labs was 33% ± 33%, with half of the analyte recoveries higher in one lab and half lower (i.e. unbiased residuals). Thus the we have excellent internal comparability and reproducibility, and acceptable comparability to BRD.

Table 4. Results and comparison of replicate analyses of a lake trout check sample.

Compounds	UMN, ng/g (n=8) *	% CV UMN	USGS-BRD, ng/g (n=?) **	% CV USGS-BRD	RPD between UMN and USGS-BRD
PCB 70+76	63	8%	71	23%	-12%
PCB 151	20	2%	23	21%	-15%
PCB 138+163	173	4%	346	21%	-67%
PCB 174	27	4%	26	15%	6%
PCB 180	88	5%	103	15%	-16%
PCB 201	36	6%	35	21%	5%
c-nonachlor	99	15%	60	52%	49%
t-nonachlor	145	8%	126	27%	14%
t-chlordane	40	47%	43	26%	-7%
c-chlordane	81	6%	Not Reported		
toxaphene	1589	24%	539	32%	99%
PeCB	1.1	7%	1.4	50%	-26%
HCB	20.1	4%	12.8	28%	44%
OCS	2.2	16%	1.8	44%	21%
Hepta Epox b	14.3	21%	24.8	25%	-53%
Oxychlordane	19.9	20%	37.7	31%	-62%
p,p-DDE	1001.0	8%	1244.8	21%	-22%
Dieldrin	116.7	18%	129.1	17%	-10%
Endrin	12.4	12%	14.8	35%	-18%
p,p-DDT	392.1	21%	98.5	20%	120%

* data surrogate corrected
** data not surrogate corrected

Accuracy – Accuracy is assessed in two ways. The first is by the recovery of surrogate standards added to each sample, and the second is by the recovery of a suite of analytes spiked into solvent and run through all procedures (spike recovery samples).

A series of 5 surrogate standards are added to every sample. Two PCB congeners (#65 and #188) not found in any Aroclor are added for assessing PCB recovery, and the stable isotopes (C-13 labeled) of HCB, lindane, DDE, and chlordane are used to assess the other analytes (see Table 3 for which compounds are assessed by which surrogates). The mean recoveries and standard deviations for all fish samples for each of the years 1999 and 2000 are shown in the table below. Mean recoveries ranged from 66% to 111% for the suite of surrogates. There were no systematic differences in recoveries between species, or between years. The C-13 chlordane, DDE, and lindane recoveries had the greatest variability (30-39% standard deviations). The percentage of recovery data meeting the quality assurance goals was 89%.

Table 5. Mean recoveries and standard deviations of suite of surrogate recovery compounds in all fish for both years.

	13C HCB	13C Lindane	13C p,p-DDE	13C chlordane (OC run)	PCB 65	PCB 188	13C chlordane (tox run)
Mean all fish, 1999	66%	81%	111%	93%	74%	78%	102%
std deviation	16%	23%	38%	32%	18%	17%	38%
Mean all fish, 2000	73%	101%	75%	108%	76%	76%	81%
std deviation	18%	31%	25%	39%	12%	11%	33%

Precision. Precision is determined from duplicate analyses of the same composite sample. There were 5 duplicate samples included in these data, and 89% of the duplicate data where both individual values passed QA met the guideline of having a relative percent difference less than 25%. The unacceptable duplicate values were somewhat randomly distributed. Analytes that failed QA in two of the samples included dieldrin, pp'-DDD, op'-DDT, and toxaphene.

Blanks. A procedural blank is included with each set of six Soxhlet extractions. To be acceptable, any analytes noted in the blanks must be below the established detection limits. In all analyses, all blanks have been found acceptable.

IV. DATA RESULTS AND OTHER GRANT ACTIVITIES

A. Emerging Contaminants Workshop

To address the concern that the analyte list of the GLFMP had not been updated in some time, Dr. Swackhamer organized a workshop for GLNPO that would inform them of the recent research on emerging contaminants with the intent of using this information to reach a consensus on changes to the GLFMP analyte list. The Workshop on Emerging Contaminants in Great Lakes Fish was held in Chicago, March 6, 2001. Five experts were invited to present their most recent research on the presence and prevalence of emerging contaminants. The goals of this workshop were to (1) provide scientific input to EPA and the states on what contaminants of present or emerging concern should be considered for inclusion in GLFMP and (2) provide scientific guidance on how to identify or anticipate potential contaminants of concern in fish tissue in the future. The invited speakers included Prof. Ron Hites, Indiana University, Dr. Ed Furlong, USGS in Denver, Dr. Cliff Rice, USDA in Maryland, Dr. Mehran Alaee, CCIW in Burlington, Ontario, and Dr. K. Kannan from Michigan State University. Participants included US EPA GLNPO staff, USGS BRD staff, and representatives from each of the Great Lakes States' fish contaminant programs. The report of this workshop is attached as an appendix. The Workshop recommended that the GLFMP be expanded to include the following additional analytes in all fish: polybrominated diphenyl ethers (PBDEs), polychlorinated naphthalenes (PCNs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), PBB-153, and mercury (Hg). These analytes met the criteria that the contaminants be found in Great Lakes fish, have known adverse health effects, and have established analytical methods. It was recommended that these contaminants be analyzed beginning with the 2000 fish collections. It was recommended that we drop dachtal and pentachlorophenyl methyl ether, as these compounds are not found in Great Lakes fish. They were included historically because they were a routine analyte of the Food and Drug Administration lab that analyzed the coho fillet composites.

B. Lake Trout Data 1999-2000

The mean values of all analytes for each year (1999 and 2000) are provided in Table 6. Concentrations are for whole lake trout and reported as ng contaminant/g fish on a wet weight basis except for AHH PCB TEQs, which are reported as pg/g wet weight. All individual concentrations were corrected to the appropriate surrogate recovery, and reviewed carefully for compliance with the QA objectives and guidelines. Mean values only include those data that passed QA review by the PI. All individual data as well as means are reported in the GLENDA database.

B.1. Concentrations 1999-2000

The GLFMP was not designed to compare concentrations of contaminants across lakes, as the fish of a constant length are not the same ages across the lakes. However, some general conclusions can be drawn. Contaminants in lake trout are generally lowest in Lake Superior and highest in Lake Michigan. Contaminant concentrations in Lake Huron and Lake Ontario are intermediate, with Huron usually lower than Ontario. This pattern is consistent with the historical and current sources of these compounds. Lake Michigan and Lake Ontario are the most impacted by development and industrial point sources and Lake Huron is less so; Lake Superior is dominated by inputs from the atmosphere. Exceptions to this are alpha-HCH and toxaphene which are greatest in Lake Superior (see below), and OCS and mirex which are greatest in Lake Ontario. The latter is likely due to a greater concentration of point sources of these compounds in the Lake Ontario basin compared to Lake Michigan.

Comparisons between lake trout and walleye should be done with extreme caution, as the two species have very different foodchains as well as other differences. Contaminants in Lake Erie walleye are generally less than those found in lake trout from the other lakes, as would be expected. An exception is the PCB concentration, which is high relative to the other contaminants. This is due to the significant point sources of PCBs that occurred historically in the Detroit River.

Specific discussions of several compounds of interest that were routinely detected follows.

Table 6. Mean concentrations for all analytes in lake trout and walleye for 1999 and 2000. All concentrations are in ng/g wet weight. An "nd" indicates the value is below detection.

Lake	Species	Yr	Statistic	Total PCBs	PeCB	HCB	alpha-HCH	Lindane	Aldrin	Dieldrin	Endrin	OCS	Mirex
Superior	LT	1999	mean	272	nd	7.4	11	1.10	nd	21	9.4	nd	nd
			95% CL	55		0.8	1.3	0.15		4.6	1.8		
			CV	33%		17%	19%	20%		36%	19%		
		2000	mean	784	nd	15	7.7	nd	nd	31	nd	6.2	nd
			95% CL	150		1.4	2.3			7.2		1.0	
			CV	29%		15%	45%			36%		25%	
Huron	LT	1999	mean	918	nd	12	2.2	nd	nd	36	nd	4.0	nd
			95% CL	86		1.0	0.3			5.1		0.88	
			CV	15%		13%	18%			23%		34%	
		2000	mean	779	nd	12	2.3	nd	nd	32	nd	2.2	nd
			95% CL	104		1.4	0.3			5.5		0.32	
			CV	21%		19%	19%			27%		21%	
Michigan	LT	1999	mean	1865	nd	15	2.5	nd	nd	96	nd	1.6	nd
			95% CL	256		2.8	0.26			7.6		0.41	
			CV	20%		29%	16%			12%		37%	
		2000	mean	1614	nd	12	1.6	nd	nd	90	nd	1.8	nd
			95% CL	92		1.5	0.3			18		0.57	
			CV	9%		19%	24%			29%		39%	
Erie	Walleye	1999	mean	569	nd	3.7	nd	nd	nd	8.7	nd	2.5	nd
			95% CL	163		1.4				0.87		1.5	
			CV	39%		45%				9%		69%	
		2000	mean	1241	nd	3.2	nd	nd	nd	12	nd	5.8	nd
			95% CL	295		0.28				1.7		1.3	
			CV	30%		11%				17%		28%	
Ontario	LT	1999	mean	1294	nd	24	3.2	nd	nd	64.4	nd	19.5	57.5
			95% CL	125		2.9	0.41			12.0		4.61	12.6
			CV	16%		19%	20%			28%		38%	34%
		2000	mean	1174	nd	19	2.6	nd	nd	45	1.1	9.6	69.1
			95% CL	116		1.5	0.5			9	0.9	1.3	14.8
			CV	16%		12%	25%			34%	131%	22%	35%

Table 6, Cont.

Lake	Species	Yr	Statistic	o,p-DDD	o,p-DDE	o,p-DDT	p,p-DDD	p,p-DDE	p,p-DDT	Sum p,p-DDE+DDT+DDD	Heptachlor	Oxychlordane
Superior	**LT**	**1999**	mean	**nd**	**nd**	**nd**	**nd**	**92**	**93**	**167**	**nd**	**nd**
			95% CL					20	42	59.1		
			CV					36%	64%	57%		
		2000	mean	**nd**	**11**	**23**	**nd**	**361**	**175**	**567**	**nd**	**19**
			95% CL		2.1	6.4		87	79	127		3.6
			CV		31%	44%		37%	69%	34%		30%
Huron	**LT**	**1999**	mean	**nd**	**nd**	**nd**	**nd**	**376**	**78**	**504**	**nd**	**14**
			95% CL					54	32	82.7		1.6
			CV					23%	59%	26%		19%
		2000	mean	**nd**	**nd**	**nd**	**nd**	**347**	**181**	**557**	**nd**	**14**
			95% CL					53	28	69		3
			CV					24%	23%	18%		22%
Michigan	**LT**	**1999**	mean	**nd**	**nd**	**nd**	**nd**	**612**	**319**	**883**	**nd**	**29**
			95% CL					109	125	134		2.3
			CV					27%	53%	23%		12%
		2000	mean	**nd**	**8.6**	**32**	**31**	**801**	**246**	**1056**	**nd**	**24**
			95% CL		1.9	5.4	7.1	84	90.4	143		5.0
			CV		30%	17%	35%	16%	56%	19%		32%
Erie	**Walleye**	**1999**	mean	**nd**	**nd**	**nd**	**nd**	**85**	**nd**	**94.9**	**nd**	**nd**
			95% CL					44		40.9		
			CV					59%		49%		
		2000	mean	**nd**	**6.0**	**nd**	**nd**	**67**	**nd**	**84.5**	**nd**	**nd**
			95% CL		1.1			11		8.04		
			CV		22%			20%		12%		
Ontario	**LT**	**1999**	mean	**nd**	**15.4**	**nd**	**nd**	**484**	**137**	**594**	**nd**	**15.6**
			95% CL		6.45			62.4	73.2	135		1.76
			CV		37%			19%	72%	33%		17%
		2000	mean	**13.2**	**7.4**	**32.1**	**34.1**	**437**	**394**	**864**	**nd**	**10.2**
			95% CL	5.2	1.8	5.86	6.37	36	134	133		0.84
			CV	60%	31%	21%	25%	13%	52%	24%		13%

Table 6, Cont.

| Lake	Species	Yr	Statistic	Heptachlor epoxide b	Heptachlor epoxide a	Toxaphene	trans-Nonachlor	cis-Nonachlor	trans-Chlordane	cis-Chlordane
Superior	**LT**	**1999**	mean	**nd**	**nd**	**673**	**33**	**17**	**4.7**	**7.4**
			95% CL			125	7.6	3.3	1.3	1.6
			CV			27%	35%	29%	43%	34%
		2000	mean	**nd**	**nd**	**2493**	**146**	**102**	**18**	**36**
			95% CL			659	36	24	6.1	6.5
			CV			40%	38%	35%	52%	27%
Huron	**LT**	**1999**	mean	**nd**	**nd**	**467**	**58**	**25**	**6.5**	**16**
			95% CL			150	9.3	4.6	1.7	2.8
			CV			46%	26%	29%	38%	28%
		2000	mean	**nd**	**nd**	**676**	**48**	**33**	**11**	**16**
			95% CL			98	11	7.0	2.4	4.0
			CV			22%	34%	33%	33%	38%
Michigan	**LT**	**1999**	mean	**16**	**11**	**813**	**122**	**66**	**34**	**41**
			95% CL	2.5	3.1	225	26	7.0	8.7	4.2
			CV	24%	19%	37%	27%	15%	37%	15%
		2000	mean	**13**	**nd**	**1123**	**138**	**72**	**22**	**47**
			95% CL	2.3		200	26	9.9	7.0	9.4
			CV	26%		27%	29%	21%	46%	30%
Erie	**Walleye**	**1999**	mean	**nd**	**nd**	**31**	**9.1**	**5.7**	**4.8**	**9.6**
			95% CL			18	6.3	0.75	2.0	5.5
			CV			66%	94%	10%	38%	50%
		2000	mean	**nd**	**nd**	**232**	**7.8**	**6.7**	**5.3**	**6.7**
			95% CL			137	0.79	1.2	1.0	0.77
			CV			74%	13%	22%	23%	15%
Ontario	**LT**	**1999**	mean	**9.70**	**nd**	**169**	**60.0**	**23.4**	**6.25**	**16.5**
			95% CL	0.942		29.4	8.65	4.30	0.486	2.97
			CV	16%		27%	22%	28%	12%	27%
		2000	mean	**nd**	**nd**	**521**	**47.3**	**29.8**	**10.8**	**21.4**
			95% CL			129	7.5	3.1	4.1	2.2
			CV			40%	26%	17%	61%	16%

Table 6, Cont.

Lake	Species	Yr	Statistic	BDE 47	BDE 66	BDE 99	BDE 100	BDE 153	BDE 154	PBB 153	Hg
Superior	**LT**	**1999**	mean								**123**
			95% CL								21
			CV								27%
		2000	mean	**79**	**3.9**	**53**	**19**	**8.8**	**16**		**433**
			95% CL	21	1.5	14	4.6	3.1	4.1		76
			CV	38%	51%	40%	36%	50%	38%		28%
Huron	**LT**	**1999**	mean	**32**	**0.7**	**7.8**	**6.5**	**1.4**	**2.0**	**2.1**	**144**
			95% CL	7.7	0.24	2.2	1.9	0.43	0.89	0.63	20
			CV	27%	39%	32%	33%	34%	51%	33%	16%
		2000	mean	**59**	**1.0**	**13**	**12**	**2.1**	**7.1**		**144**
			95% CL	13	0.65	1.7	2.9	0.79	1.4		18
			CV	26%	55%	15%	27%	55%	31%		20%
Michigan	**LT**	**1999**	mean								**127**
			95% CL								8.8
			CV								11%
		2000	mean	**228**	**3.7**	**48**	**45**	**11**	**19**		**146**
			95% CL	82	1.4	16	13	4.2	7.1		18
			CV	45%	48%	40%	35%	47%	47%		20%
Erie	**Walleye**	**1999**	mean								**124**
			95% CL								37
			CV								41%
		2000	mean	**32**	**nd**	**5.9**	**7.8**	**2.6**	**2.4**		**114**
			95% CL	7.88		1.8	1.9	1.5	0.9		11
			CV	30%		38%	30%	75%	46%		12%
Ontario	**LT**	**1999**	mean								**123**
			95% CL								8.5
			CV								11%
		2000	mean	**144**	**2.4**	**34**	**24**	**10**	**13**		**115**
			95% CL	38	0.7	13	9.2	2.7	4.9		15
			CV	35%	37%	50%	51%	36%	49%		21%

PCBs. The PCB concentrations were lowest in Lake Superior (272 and 784 ng/g in 1999 and 2000) and greatest in Lake Michigan (1841 and 1614 ng/g in 1999 and 2000) which is consistent with previous data (e.g. DeVault et al. 1996). The significant differences in concentrations in Lakes Superior and Lake Erie between 1999 and 2000 are highly unlikely due to lake-wide differences between years, but rather due to differences between sites and/or populations of fish. In Lake Superior, there is variation of this order within the same site across a two year period, so it is more likely that is it is due to the collection of different subpopulations. Different subpopulations may have different concentrations if some subpopulations are native and others are from stocks. The stocked fish would have had different exposures in the hatcheries, leading to differences as fry. It is also possible that different populations (stocked or not) may have different foodwebs. For example, some populations may feed more on pelagic species, and another population may have more benthic prey. These dietary differences would result in different contaminant concentrations, as the concentration of prey is what controls the concentrations in top predators (Thomann and Connolly 1984; Thomann et al. 1992). The lake trout of this size class in Lake Superior are typically 8-10 years old, and thus the concentrations represent an integration of the contaminant over several years' time. There is no known possible mechanism that could increase the concentrations by factors of 2 or 3 over a one- or two-year time frame in the absence of a massive input of PCBs. Furthermore, this pattern of higher concentrations in 2000 compared to 1999 is seen in nearly every analyte that was detected, not just PCBs. Thus we conclude that the differences between years are a result of real differences between populations of lake trout within Lake Superior, and not due to differences between years in contaminants in the lake as a whole.

In Lake Erie, PCB concentrations are greater in western basin sediments compared to the eastern basin (Marvin et al. 2002), and this gradient may be reflected in the walleye collected from those regions. While walleye are known to migrate throughout the lake, the collections made in these years may be more representative of the local environment. These differences are not seen for other contaminants, which is consistent with the fact that PCBs have several point sources in the Detroit River and western basin thus creating the gradient, while other contaminants do not have the same well defined gradients.

The PCB congener pattern was compared across years, lakes, and fish species. There were no differences in the pattern, which is dominated by the penta-, hexa, and hepta-chlorinated congeners (see Figure 1).

Figure 1. PCB homologue composition for all fish, all lakes, in 1999 and 2000.
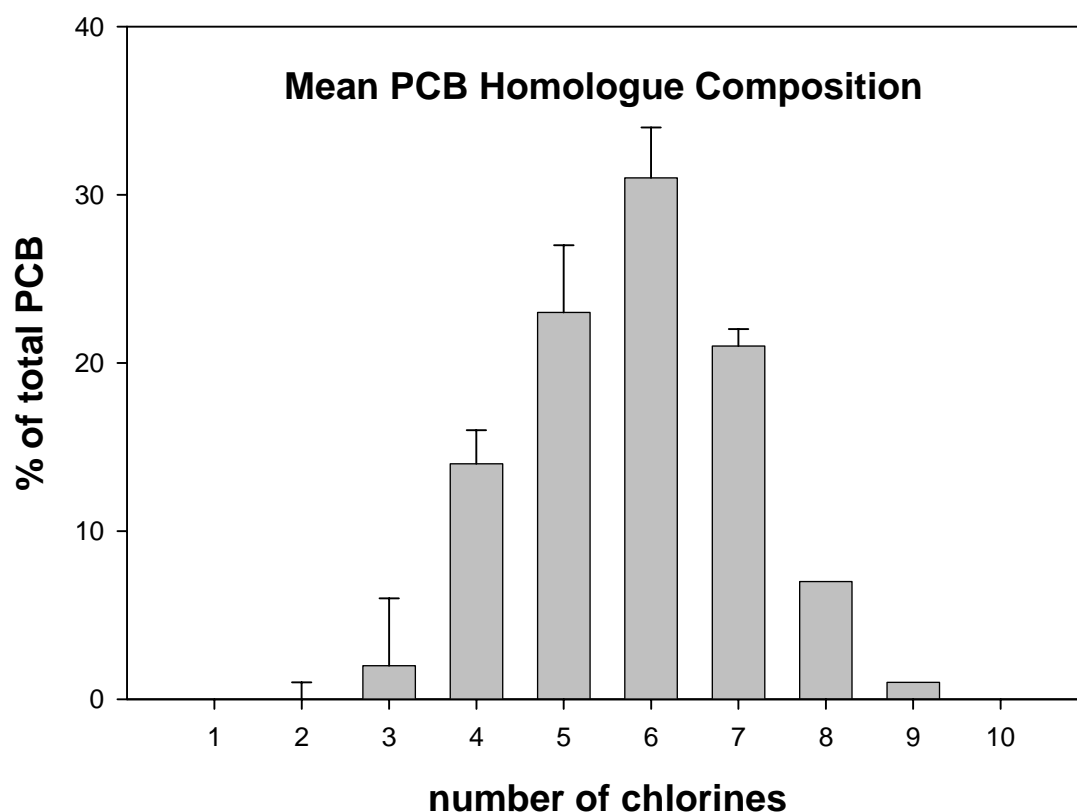
AHH PCB TEQs. The TEQs for the lake trout ranged from 8.7 ppt in Lake Michigan to 0.74 ppt in Lake Superior. TEQs in Lake Huron and Lake Ontario were both approximately 4 ppt. The TEQs in Lake Erie walleye averaged 0.04 ppt.

DDT. The DDT components of interest are the p,p'-substituted compounds, and concentrations in lake trout are dominated by p,p'-DDE. On average, p,p'-DDT is expected to contribute approximately 10-30% of the total, but our data for this compound are not always consistent with this expectation. In particular, Lake Superior in 1999 and Lake Ontario in 2000 show higher than expected levels of DDT. This may reflect real differences in the foodwebs at these sites, or may be due to a laboratory procedure. This is being thoroughly investigated at this

time; regardless, the data for ∑DDT (sum of p,p-DDE, DDT, and DDD) is considered to be valid. The contribution of DDD is negligible in all lakes and is usually below detection.

Concentrations of ∑DDT in lake trout were lowest in Lake Superior (167 and 567 ng/g in 1999 and 2000) which was similar to Lake Huron (504 and 557 ng/g in 1999 and 2000) and Lake Ontario (594 and 864 ng/g in 1999 and 2000). Concentrations were highest in Lake Michigan (883 and 1056 ng/g in 1999 and 2000). Concentrations in Lake Erie walleye were lower than in lake trout (95 and 85 ng/g in 1999 and 2000). The discussion of differences between years in Lake Superior found above for PCBs applies to DDE as well.

Dieldrin. Concentrations for dieldrin in lake trout ranged from a low of 21 and 31 ng/g in Lake Superior for the two years to a high of 94 and 90 ng/g in Lake Michigan. Concentrations in Lake Erie walleye were lower still, ranging from 9-12 ng/g.

Toxaphene, alpha-HCH. Concentrations of toxaphene and alpha-HCH are greatest in Lake Superior. Toxaphene in lake trout were 673 and 2490 ng/g in Lake Superior for the two years, and lowest in Lake Ontario (169-521 ng/g). Concentrations in walleye were lower still. The reasons for this are because the lakes all reached equilibrium with the atmosphere in the 1980's but Lake Superior is losing toxaphene at a much slower rate via volatilization and sedimentation than the other lakes due to its larger volume, lower productivity, and colder temperatures (Swackhamer et al. 1998, 1999). Thus the water concentrations of toxaphene are greater than those in the other lakes, and the fish reflect the water (Glassmeyer et al. 1997). Toxaphene behaves this way because it has a higher vapor pressure and solubility than other bioaccumulative organochlorines. Alpha-HCH also has a high relative vapor pressure and solubility, and thus it is logical that it would greater in Lake Superior fish.

Nonachlors and Chlordanes. In general, t-nonachlor was the most prevalent of these compounds, followed by c-nonachlor, oxychlordane, c-chlordane, and t-chlordane. T-nonachlor ranged from a high of 131-136 ng/g in Lake Michigan lake trout to less than half that value in the other lakes' trout. Although t-nonachlor was a minor component of the technical chlordane mixture, it is the least metabolized and predominates within the food web.

HCB. This compound is one of the most widely used organochlorine compounds in history, and is still in active commerce. Concentrations are similar in lake trout across the lakes, ranging from 7-25 ng/g. This pattern indicates that the atmosphere may be the dominant source to all the lakes.

OCS and Mirex. Concentrations of OCS are greatest in Lake Ontario lake trout (10-20 ng/g), but found in concentrations ranging from 1-6 ng/g in the other lakes' trout. This may reflect the historic points sources of OCS to Lake Ontario. Mirex is detected only in Lake Ontario lake trout, a clear reflection of the point sources of mirex in the 1970s to this lake.

Mercury. Concentrations of mercury are similar across all fish from all lakes. Interestingly, this includes Lake Erie walleye, possibly due to the difference in factors that control mercury bioaccumulation compared to that of organochlorine compounds. Concentrations were generally 110-150 ng/g, with the exception of the Lake Superior 2000 fish which were 415 ng/g. This is consistent with the increase in most other contaminants, as discussed above. Furthermore, mercury concentrations in Lake Superior lake trout have been reported to have similar concentrations as these (Pat McCann, Minnesota Department of Health, personal communication).

PBDEs. This analyte was added in 2000. However, the standards for this compound were delayed from the manufacturer, and many fish were already extracted by the time the standards arrived. Thus a combination of some of the 1999 and 2000 fish were analyzed for a suite of PBDE congeners. Concentrations of the PBDE congeners were in the relative order 47>100=99>153=154>66. Concentrations were greatest in lake trout from Lake Michigan, followed by those from Lake Ontario and Lake Superior. Lake Huron lake trout had the lowest concentrations, and the data from both 1999 and 2000 was comparable. These data are comparable to those reported for other fish from the Great Lakes (Manchester-Neesvig et al., 2001, Hites 2004). PBB-153 was found in the 1999 Lake Huron lake trout at 1.4 ng/g and in Lake Ontario at 2.8 ng/g; the other composites were not analyzed due to a delay in receiving the analytical standard.

Compounds Not Detected: Compounds that were rarely or never detected in fish included pentachlorbenzene, lindane, aldrin, endrin, the o,p-substituted DDT family of compounds, p,p'-DDD, heptachlor, heptachlor epoxide, PCNs, and PCDD/Fs. It is recommended that these compounds should be removed from the monitoring list.

B.2 Time Trends of Selected Contaminants

The GLFMP was designed to assess time trends in contaminants by comparing the same sites over time. The time trends in previous interpretations have focused on the even year data, and we will continue this approach. The discussion of trends will be submitted as an addendum to this Report, as the complete historical dataset needed for a thorough discussion of this matter are not yet available.

C. Chinook Data 1999

The data for the 1999 Chinook are summarized in Table 7, below. The analyte concentrations are reported as site means. Within a lake, the Lake Huron Swan River Chinook always had greater concentrations of analytes than the Au Sable Chinook (2-3 times greater), as did the Lake Erie Trout Run steelhead compared to the Lake Erie Grand River steelhead. Lake Superior French River Chinook were consistently greater in concentrations than Pikes Creek Chinook. There was a trend for the Lake Michigan Grand River fish to have greater concentrations than other sites, although differences were small.

The PCB concentrations in Chinook were lowest in Lake Superior (159-233 ng/g) and higher in Lakes Michigan (756-1267 ng/g) and Ontario (906 ng/g), with intermediate values in Lake Huron (433-1161 ng/g) and Lake Erie steelhead trout (365-498 ng/g). The ∑DDT followed a similar pattern except that Lake Erie steelhead had concentrations on the order of Lake Superior. The range in values is consistent with the fact that PCBs and DDT have had a mixture of both atmospheric and non-atmospheric sources. Conversely, HCB and dieldrin concentrations were similar across the lakes and averaged approximately 4 ng/g and 14 ng/g, respectively. Octachlorostyrene ranged from 1.8-2.0 ng/g, except for Lake Ontario which had substantially greater concentrations (10 ng/g). Lake Ontario also had the only detectable concentrations of mirex (54 ng/g), as expected due to its source profile. Toxaphene was highest in Lake Superior, followed by Lake Michigan, Lake Huron, Lake Ontario, and Lake Erie, similar to the pattern seen for lake trout. Concentrations ranged from 10 – 397 ng/g. The chlordanes and nonachlors all were greatest in Lake Michigan, followed by similar levels in Lake Huron and Lake Ontario, followed by Lake Superior and Lake Erie steelhead. As seen in other species, the nonachlors dominated the chlordane components.

The following compounds were below detection, and should be considered for elimination from the monitoring program: pentachlorobenzene, a-HCH and lindane, aldrin, endrin, heptachlor and both of the epoxides, oxychlordane, and all o,p-DDT components.

Table 7. Mean values for analytes for Chinook salmon and/or steelhead trout from 1999.
All concentrations are in ng/g wet weight. An "nd" means the value was below detection.

Species	Site	Lake	Statistic	Total PCBs	PeCB	HCB	alpha-HCH	Lindane	Aldrin	Dieldrin
Chinook	Pike's Creek	Superior	mean	159	nd	4.8	1.5	nd	nd	13
			CV	10%		8.4%	12%			35%
			95% CL	17		0.46	0.24			5.0
Chinook	French R	Superior	mean	233	nd	5.9	nd	nd	nd	15
			CV	13%		14%				4.1%
			95% CL	34		0.95				0.71
Chinook	St Joseph R.	Michigan	mean	780	nd	4.1	2.4	nd	nd	19
			CV	4.4%		5.5%				19%
			95% CL	39		0.26				4.0
Chinook	Platte R.	Michigan	mean	1037	nd	4.0	nd	nd	nd	24
			CV	38%		22%				54%
			95% CL	445		1.0				15
Chinook	Grand R.	Michigan	mean	1267	nd	3.8	nd	nd	nd	17
			CV	13%		1.3				3.1%
			95% CL	189		34%				0.58
Chinook	Trail Creek	Michigan	mean	756	nd	1.8	13	1.2	nd	18
			CV	16%		4.7%		23%		9.4%
			95% CL	140		0.23		0.37		2.4
Chinook	Root R.	Michigan	mean	863	nd	3.1	nd	nd	nd	16
			CV	5.9%		42%				16%
			95% CL	57		1.5				2.9
Chinook	Thompson Cr.	Michigan	mean	1053	nd	3.5	nd	nd	nd	7.8
			CV	22%		33%				28%
			95% CL	267		1.3				2.5

Table 7., cont

Species	Site	Lake	Statistic	Heptachlor	Heptachlor epox b	Heptachlor epox a	Oxychlordane
Chinook	Pike's Creek	Superior	mean	nd	nd	nd	nd
			CV				
			95% CL				
Chinook	French R	Superior	mean	nd	nd	nd	nd
			CV				
			95% CL				
Chinook	St Joseph R.	Michigan	mean	nd	nd	nd	nd
			CV				
			95% CL				
Chinook	Platte R.	Michigan	mean	nd	nd	nd	14
			CV				
			95% CL				
Chinook	Grand R.	Michigan	mean	nd	nd	nd	11
			CV				15%
			95% CL				2.3
Chinook	Trail Creek	Michigan	mean	nd	nd	nd	nd
			CV				
			95% CL				
Chinook	Root R.	Michigan	mean	nd	nd	nd	10
			CV				
			95% CL				
Chinook	Thompson Cr.	Michigan	mean	nd	nd	nd	nd
			CV				
			95% CL				

Table 7., cont

Species	Site	Lake	Statistic	o,p-DDD	o,p-DDE	o,p-DDT	p,p-DDD	p,p-DDE	p,p-DDT	Sum p,p-DDE+DDT+DDD
Chinook	Pike's Creek	Superior	mean	nd	nd	nd	nd	45	nd	49
			CV					3.5%		6.1%
			95% CL					1.8		3.4
Chinook	French R	Superior	mean	nd	nd	nd	nd	59	nd	63
			CV					11%		11%
			95% CL					7.5		7.9
Chinook	St Joseph R.	Michigan	mean	nd	nd	nd	nd	382	38	429
			CV					7.1%	22%	6.7%
			95% CL					31	10	32
Chinook	Platte R.	Michigan	mean	nd	17	nd	25	540		556
			CV					59%		57%
			95% CL					359		356
Chinook	Grand R.	Michigan	mean	nd	13	43	99	565	38	558
			CV					26%	35%	26%
			95% CL					168	18	203
Chinook	Trail Creek	Michigan	mean	nd	nd	nd	nd	317	26	320
			CV					13%	10%	16%
			95% CL					45	2.8	59
Chinook	Root R.	Michigan	mean	nd	nd	nd	nd	456	30	494
			CV					12%	20%	12%
			95% CL					63	6.8	68
Chinook	Thompson Cr.	Michigan	mean	nd	nd	nd	nd	518	33	557
			CV					21%	45%	23%
			95% CL					124	17	142

Table 7., cont

Species	Site	Lake	Statistic	Endrin	OCS	Mirex	Toxaphene	trans-Nonachlor	cis-Nonachlor	trans-Chlordane	cis-Chlordane
Chinook	Pike's Creek	Superior	mean	nd	3.6	nd	376	21	10	3.4	4.5
			CV		71%		7.7%	13%	13%	2.8%	16%
			95% CL		3.6		33	3.2	1.4	0.11	0.80
Chinook	French R	Superior	mean	nd	1.8	nd	417	26	12	3.7	5.1
			CV				17%	15%	14%	17%	27%
			95% CL				80	4.4	1.9	0.72	1.5
Chinook	St Joseph R.	Michigan	mean	nd	nd	nd	311	60	25	7.4	11
			CV				16%	10%	6.6%	3.0%	9.4%
			95% CL				55	6.7	1.9	0.25	1.2
Chinook	Platte R.	Michigan	mean	nd	1.8	nd	391	86	40	7.9	14
			CV				22%	35%	43%	24%	24%
			95% CL				99	34	20	2.2	3.8
Chinook	Grand R.	Michigan	mean	nd	nd	nd	367	96	44	14	17
			CV				7.9%	10%	20%	47%	8.0%
			95% CL				33	11	10	7.5	1.5
Chinook	Trail Creek	Michigan	mean	55	nd	nd	240	51	22	6.3	9.1
			CV				3.5%	13%	6.7%	7.6%	11%
			95% CL				10	7.4	1.6	0.54	1.1
Chinook	Root R.	Michigan	mean	nd	2.0	nd	186	66	28	6.9	12
			CV		28%		3.3%	10%	17%	5.5%	3.7%
			95% CL		0.6		6.8	7.4	5.4	0.43	0.5
Chinook	Thompson Cr.	Michigan	mean	nd	1.6	nd	191	72	31	5.9	12
			CV		0.6%		25%	22%	24%	24%	27%
			95% CL		0.01		55	18	8.5	1.6	3.8

Table 7., Cont.										
Species	Site	Lake	Statistic	Total PCBs	PeCB	HCB	alpha-HCH	Lindane	Aldrin	Dieldrin
Chinook	Swan R.	Huron	mean	1161	nd	3.6	nd	nd	nd	16
			CV	64%		4.2%				2.8%
			95% CL	845		0.17				0.50
Chinook	Au Sable	Huron	mean	433	nd	2.6	29	nd	nd	6.7
			CV	21%		17%				3.9%
			95% CL	104		0.60				0.37
Steelhead	Grand R.	Erie	mean	365	nd	2.8	nd	nd	nd	8.3
			CV	40%		6.5%				6.5%
			95% CL	164		0.25				0.7
Steelhead	Trout Run	Erie	mean	498	nd	4.8	nd	nd	nd	14
			CV	13%		28%				27%
			95% CL	71		1.5				4.3
Chinook	Salmon Hatchery	Ontario	mean	906	nd	5.8	nd	nd	nd	6.7
			CV	28%		18%				22%
			95% CL	291		1.2				1.6

Table 7., Cont.							
Species	**Site**	**Lake**	**Statistic**	**Heptachlor**	**Heptachlor epox b**	**Heptachlor epox a**	**Oxychlordane**
Chinook	Swan R.	Huron	mean	**nd**	**nd**	**nd**	**nd**
			CV				
			95% CL				
Chinook	Au Sable	Huron	mean	**nd**	**nd**	**nd**	**nd**
			CV				
			95% CL				
Steelhead	Grand R.	Erie	mean	**nd**	**nd**	**nd**	**nd**
			CV				
			95% CL				
Steelhead	Trout Run	Erie	mean	**nd**	**nd**	**nd**	**nd**
			CV				
			95% CL				
Chinook	Salmon Hatchery	Ontario	mean	**nd**	**nd**	**nd**	**nd**
			CV				
			95% CL				

Species	Site	Lake	Statistic	o,p-DDD	o,p-DDE	o,p-DDT	p,p-DDD	p,p-DDE	p,p-DDT	Sum p,p-DDE+DDT+DDD
Table 7., Cont.										
Chinook	Swan R.	Huron	mean	nd	nd	nd	nd	364	27	394
			CV					12%	18%	10%
			95% CL					48	5.4	44
Chinook	Au Sable	Huron	mean	nd	nd	nd	nd	175	26	196
			CV					23%	23%	29%
			95% CL					45	8.2	64
Steelhead	Grand R.	Erie	mean	nd	nd	nd	nd	26	nd	29
			CV					23%		23%
			95% CL					8.1		9.3
Steelhead	Trout Run	Erie	mean	nd	nd	nd	nd	48	nd	54
			CV					20%		21%
			95% CL					11		13
Chinook	Salmon Hatchery	Ontario	mean	nd	nd	nd	nd	360	49	425
			CV					34%	39%	34%
			95% CL					137	22	163

Table 7., Cont.											
Species	**Site**	**Lake**	**Statistic**	**Endrin**	**OCS**	**Mirex**	**Toxaphene**	**trans-Nonachlor**	**cis-Nonachlor**	**trans-Chlordane**	**cis-Chlordane**
Chinook	Swan R.	Huron	mean	**nd**	**nd**	**nd**	**125**	**45**	**17**	**5.6**	**10**
			CV				31%	25%	20%	17%	22%
			95% CL				43	13	3.9	1.1	2.4
Chinook	Au Sable	Huron	mean	**nd**	**1.9**	**nd**	**86**	**31**	**12**	**3.4**	**5.4**
			CV		18%		21%	19%	15%	38%	28%
			95% CL		0.49		21	6.5	2.1	1.5	1.7
Steelhead	Grand R.	Erie	mean	**nd**	**nd**	**nd**	**nd**	**8.0**	**2.8**	**1.8**	**3.4**
			CV					50%	18%		17%
			95% CL					4.6	0.69		0.8
Steelhead	Trout Run	Erie	mean	**nd**	**1.9**	**nd**	**14**	**10**	**4.9**	**3.7**	**6.4**
			CV		24%		41%	40%	29%	13%	21%
			95% CL		0.5		8.0	4.5	1.6	0.53	1.5
Chinook	Salmon Hatchery	Ontario	mean	**nd**	**10**	**54**	**81**	**35**	**15**	**2.7**	**6.5**
			CV		16%	23%	39%	30%	27%	19%	21%
			95% CL		1.7	14	36	12	4.6	0.6	1.5

D. Coho Data 2000

The contaminants in adult coho (greater than 500 mm) are summarized in Table 8 below, by both lake and site. Only fish greater than 500 mm in length were included in these means, to not bias them low by including fish that are only 1-2 yrs of age. There were no systematic differences among sites in the Lake Michigan coho data, with the exception that the Kewaunee fish had a 25-50% greater concentration of PCBs, DDT components and sum, and PBDEs than the other sites. Total PCBs were approximately 0.5 ug/g in coho from both Lake Michigan and Lake Erie, and slightly higher in Lake Huron Chinook. This is expected, as the Chinook are older than the coho and have had longer exposures. Concentrations of hexachlorobenzene (2.2-3.0 ng/g), dieldrin (6.4-10 ng/g), t-chlordane (3.1-4.5 ng/g), c-chlordane (5.7-10 ng/g), and mercury (124-127 ng/g) were very similar in coho from both Lakes Michigan and Erie. Concentrations of other contaminants were significantly greater in Lake Michigan compared to those in Lake Erie. These included p,p-DDE+DDT+DDD (~five times greater), toxaphene (~twice as great), c- and t-nonachlor (~3 times greater), PBDE congeners (~4-6 times greater) and PBB-153 (~10 times greater). For these contaminants, the Chinook concentrations in Lake Huron were usually always slightly greater than those in Lake Michigan coho.

The coho data from Lake Michigan are sufficiently robust in degrees of freedom and in quality that trends over time are possible to determine. This analysis and discussion will be reported as an addendum to this report when accurate historical data are available.

Table 8. Mean concentrations of all analytes for coho and Chinook salmon from 2000.
An "nd" indicates value was below detection; "na" indicates that the sample was not analyzed.

Species	Lake	Site	Statistic	Total PCBs	PeCB	HCB	alpha-HCH	Lindane	Aldrin	Dieldrin
Coho	Erie	Trout Run	mean	473	nd	2.6	nd	nd	nd	6.4
			95% CL	33		0.5				2.3
			CV	6%		15%				32%
Coho	Michigan	Kewaunee R	mean	649	nd	3.0	nd	nd	nd	8.4
			95% CL	35		0.13				1.7
			CV	4%		3.2%				14%
	Michigan	Trail Cr	mean	463	nd	2.8	nd	nd	nd	10
			95% CL	68		0.33				1.7
			CV	11%		8.3%				13%
	Michigan	Thompson Cr	mean	450	nd	2.2	nd	nd	nd	10
			95% CL	35		0.02				2.2
			CV	6%		0.73%				16%
	Michigan	Grand R	mean	581	nd	2.7	nd	nd	nd	7.4
			95% CL	80		0.98				2.0
			CV	10%		26%				19%
Chinook	Huron	Swan R	mean	719	nd	3.8	nd	nd	nd	16
			95% CL	270		0.70				11
			CV	33%		16%				63%

Table 8., cont.

Species	Lake	Site	Statistic	o,p-DDD	o,p-DDE	o,p-DDT	p,p-DDD	p,p-DDE	p,p-DDT	Sum p,p-DDE+DDT+DDD
Coho	Erie	Trout Run	mean	nd	nd	nd	nd	44	nd	52
			95% CL					4.3		6.7
			CV					8.6%		11%
Coho	Michigan	Kewaunee R	mean	nd	nd	4.9	12	274	35	321
			95% CL			0.35	3.4	3.5	10	10
			CV			5.1%	21%	0.91%	21%	2.3%
	Michigan	Trail Cr	mean	nd	nd	nd	nd	187	12	203
			95% CL					26	24	58
			CV					10%	141%	20%
	Michigan	Thompson Cr	mean	nd	nd	3.6	5.3	206	16	227
			95% CL			0.83	1.0	23	14	38
			CV			17%	14%	8.1%	64%	12%
	Michigan	Grand R	mean	nd	nd	nd	6.9	259	12	278
			95% CL				1.4	70	23	49
			CV				14%	20%	141%	13%
Chinook	Huron	Swan R	mean	nd	nd	nd	nd	268	94	362
			95% CL					117	56	130
			CV					38%	52%	32%

Table 8., cont.

Species	Lake	Site	Statistic	Heptachlor	Heptachlor epoxide b	Heptachlor epoxide a	Oxychlordane	Endrin	OCS	Mirex
Coho	Erie	Trout Run	mean	nd	nd	nd	nd	nd	2.0	nd
			95% CL						0.21	
			CV						9.1%	
Coho	Michigan	Kewaunee R	mean	nd	nd	nd	3.1	nd	nd	nd
			95% CL				0.24			
			CV				5.6%			
	Michigan	Trail Cr	mean	nd	nd	nd	2.6	nd	nd	nd
			95% CL				0.39			
			CV				11%			
	Michigan	Thompson Cr	mean	nd	nd	nd	2.7	nd	nd	nd
			95% CL				0.41			
			CV				11%			
	Michigan	Grand R	mean	nd	nd	nd	3.0	nd	nd	nd
			95% CL				0.16			
			CV				3.8%			
Chinook	Huron	Swan R	mean	nd	nd	nd	nd	nd	nd	nd
			95% CL							
			CV							

Table 8., cont.

Species	Lake	Site	Statistic	Toxaphene	trans-Nonachlor	cis-Nonachlor	trans-Chlordane	cis-Chlordane
Coho	**Erie**	**Trout Run**	**mean**	**107**	**9.4**	**4.9**	**3.1**	**5.7**
			95% CL	39	2.7	1.4	0.57	1.7
			CV	32%	25%	25%	16%	27%
Coho	**Michigan**	**Kewaunee R**	**mean**	**202**	**27**	**12**	**3.8**	**8.7**
			95% CL	10	3.8	0.80	0.23	1.4
			CV	3.7%	10%	4.7%	4.4%	11%
	Michigan	**Trail Cr**	**mean**	**199**	**20**	**10**	**3.2**	**7.1**
			95% CL	5.8	0.38	1.1	0.09	0.01
			CV	2.1%	1.4%	8.2%	2.0%	0%
	Michigan	**Thompson Cr**	**mean**	**176**	**26**	**11**	**3.7**	**8.6**
			95% CL	20	3.5	0.71	0.13	1.6
			CV	8.2%	10%	4.8%	2.5%	14%
	Michigan	**Grand R**	**mean**	**191**	**33**	**14**	**4.5**	**10**
			95% CL	15	0.54	0.46	0.26	0.9
			CV	5.6%	1.2%	2.4%	4.2%	6.8%
Chinook	**Huron**	**Swan R**	**mean**	**395**	**49**	**29**	**5.0**	**11**
			95% CL	318	15	19	0.86	2.1
			CV	71%	27%	57%	15%	16%

Table 8., cont.

Species	Lake	Site	Statistic	BDE 47	BDE 66	BDE 99	BDE 100	BDE 153	BDE 154	Hg
Coho	Erie	Trout Run	mean	9.5	nd	1.5	1.9	0.79	1.2	127
			95% CL	0.88		0.32	0.18	0.41	0.17	5.1
			CV	8.1%		19%	8.4%	46%	12%	3.6%
Coho	Michigan	Kewaunee R	mean	57	nd	15	12	4.9	5	121
			95% CL	5.7		2.4	2.8	10	11	2.9
			CV	7.3%		12%	16%	141%	141%	1.8%
	Michigan	Trail Cr	mean	33	nd	4.4	3.6	nd	nd	125
			95% CL	5.1		8.7	7.0			4.9
			CV	11%		141%	141%			2.8%
	Michigan	Thompson Cr	mean	35	nd	10	7.9	nd	nd	126
			95% CL	6.1		2.3	0.48			20
			CV	13%		16%	4%			11%
	Michigan	Grand R	mean	25	nd	9.3	5.6	nd	nd	125
			95% CL							
			CV							
Chinook	Huron	Swan R	mean	54	2.3	24	13	5.4	6.0	na
			95% CL	36	1.9	10	6.4	3.8	3.8	
			CV	59%	73%	37%	45%	63%	55%	

E. Evaluating Fish for New Contaminants

Methods.   A 40.92 g sample of a Lake Ontario lake trout composite was extracted in the same manner as previous samples. Due to the high lipid content, several alumina clean-up columns were used, followed by a final lipid clean-up using a gel permeation chromatography column filled with SX-3 Bio-Beads. A previous experiment using a fractionation column of alumina and silica was deemed unnecessary for the tests that were to be done on this sample. The sample was reduced using a gentle stream of purified nitrogen and an internal standard of PCB 204 was added. The sample was run in both scan and SIM methods on a 5890 gas chromatograph coupled to a 5972 mass spectrometer in EI mode and on a 5890 gas chromatograph coupled to a 5988 mass spectrometer in ECNI mode. An EPA/NIST/NIH mass spectral library was utilized for the library searches. Authentic standards were used for compound verifications. The internal standard was used as a retention time marker and the retention time indices aided in the identification of compounds.

Results. During data acquisition of the PBDEs, several other brominated peaks were identified. Along with the six most commonly identified PBDEs (congeners 47, 66, 99, 100, 153, 154), seven other peaks were verified as PBDEs through use of a PBDE standard. The peaks were identified as BDE 28/33 (coelution), BDE 37, BDE 49, BDE 119, BDE 116, BDE 85, and BDE 126/155 (coelution). The concentration range of these compounds was from 20 pg/g ww – 1060 pg/g ww. After these compounds were identified, other brominated peaks remained unknown. One of the peaks was identified as PBB #153 at a concentration of 2.8 ng/g. Hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) are brominated compounds that have been found in the environment and both were analyzed for in the Lake Ontario fish extract. None of the brominated peaks corresponded to HBCD. A contaminant peak in the TBBPA standard matched one of the peaks in the sample; however, subsequent examination ruled out the presence of TBBPA itself. Approximately five brominated peaks remained unidentified.

The Lake Ontario lake trout extract was analyzed for the presence of polychlorinated naphthalenes (PCNs), dacthal, chlorothalonil and four alkylphenol ethoxylates (APEOs). PCN 42 and PCN 66/67 (coelution) were found at concentrations of 312 pg/g ww and 9.7 pg/g ww, respectively. However, routine extractions of fish are only 2-4 g of wet tissue, and thus PCNs are well below detection limits. Dacthal was identified at a concentration of 104 ng/g ww.

Chlorothalonil was not present in the sample. Nonylphenol mono- and di- ethoxylate (NP1EO and NP2EO) and octylphenol (OP) were not found in the sample. Traces of nonylphenol (NP) were detected. Due to the multiple isomers of NP, definite identification of specific NP peaks in the sample requires further analysis.

Additional unknown compounds present in the sample were searched for using scan methods in both ECNI and EI modes. Other than the brominated peaks previously discussed, no other emerging contaminant peaks found in the ECNI mode were present with enough mass spectral data to be identified. A library search was performed on the EI scan of the extract. No emerging contaminant peaks were identified.

PFOS. PFOS was found in all fish tested, which included 2 composites from lakes Superior, Michigan, and Ontario from 2000. Concentrations ranged from approximately 13 ng/g in Lake Superior lake trout to 35 ng/g in those from lakes Michigan and Ontario.

VI. LIST OF WORK PRODUCTS

QAPP

Workshop and its Proceedings

Updated analyte list

Data for 1999 and 2000 submitted to GLENDA

Report on 1999-2000 concentrations

Updated report on time trends (to be added as addendum)

Evaluation of fish for new contaminants

VII. REFERENCES

Cook, P. M., E. W. Zabel and R. E. Peterson (1997). The TCDD toxicity equivalence approach for characterizing risks for early life-stage mortality in trout. <u>Chemically induced alterations in functional development and reproduction of fishes</u>. R. M. Rolland, M. Gilbertson and R. E. Peterson, SETAC Press.

Cook, P.M., Robbins, J.A., Endicott, D.D., Lodge, K.B., Guiney, P.D., Walker, M.K., Zabel, E.W. and Peterson, R.E., 2003. Effects of aryl hydrocarbon receptor-mediated early life stage toxicity on lake trout populations in Lake Ontario during the 20th century. *Environmental Science & Technology* 37(17), 3864-3877.

De Vault, D. S. (1984). Contaminant analysis of fish from Great Lakes harbors and tributary mouths. U.S. Environmental Protection Agency, Great Lakes National Program Office. EPA 905/3-84-003.

De Vault, D. S. (1985). Contaminants in fish from Great Lakes harbors and tributary mouths. *Arch. Environ. Contam. Toxicol.* 14: 587-594.

De Vault, D. S., P. Bertram, D. M. Whittle and S. Rang (1995). Toxic contaminants in the Great Lakes. <u>State of the Great Lakes Ecosystem Conference (SOLEC)</u>. Chicago and Toronto, U.S. Environmental Protection Agency, Great Lakes National Program Office and Environment Canada.

De Vault, D. S., R. Hesselberg, P. W. Rodgers and T. J. Feist (1996). Contaminant trends in lake trout and walleye from the Laurentian Great Lakes. *J. Great Lakes Res.* 22: 884-895.

De Vault, D. S., P. McCann, D. L. Swackhamer, D. Helwig and G. Flom (1998). Contaminants in lake trout and sculpin from Lake Superior. Minnesota Pollution Control Agency. .

De Vault, D. S. and J. A. Weishaar (1983). Contaminant analysis of 1981 fall run coho salmon. U.S. Environmental Protection Agency, Great Lakes National Program Office. EPA 905/3-83-001.

De Vault, D. S. and J. A. Weishaar (1984). Contaminant analysis of 1982 fall run coho salmon. U.S. Environmental Protection Agency, Great Lakes National Program Office. EPA 905/3-85-004.

De Vault, D. S., J. A. Weishaar, J. M. Clark and G. Lavhis (1988). Contaminants and trends in fall run coho salmon. *J. Great Lakes Res.* 14: 23-33.

De Vault, D. S., W. A. Willford, R. Hesselberg, E. Nortrupt and E. Rundberg (1985). Contaminant trends in lake trout (Salvelinus namaycush) from the upper Great Lakes. *Arch. Environ. Contam. Toxicol.* 15: 349-356.

De Vault, D. S., W. A. Willford, R. J. Hesselberg and D. A. Nortrupt (1986). Contaminant trends in lake trout (Salvelinus namaycush) from the upper Great Lakes. *Arch. Environ. Contam. Toxicol.* 15: 349-356.

Eby, L. A., C. A. Stow, R. J. Hesselberg and J. F. Kitchell (1997). Modeling changes in growth and diet on polychlorinated biphenyl bioaccumulation in "Coregonus hoyi". *Ecol.Appl.* 7(3): 981-990.

Glassmeyer, S. T., D. S. De Vault, T. R. Myers and R. A. Hites (1997). Toxaphene in Great Lakes fish: a temporal, spatial, and trophic study. *Environ. Sci. Technol.* 31: 84-88.

Glassmeyer, S. T., K. E. Shanks and R. A. Hites (1999). Automated toxaphene quantitation by GC/MS. *Anal. Chem.* in press.

Hornbuckle, K.D., Sweet, C.W., Pearson, R.F., Swackhamer, D.L. and Eisenreich, S.J., 1995. Assessing annual water-air fluxes of polychlorinated biphenyls in Lake Michigan. *Environ. Sci. Technol.* 29(4), 869-877.

Jackson, L. J. and D. E. Schindler (1996). Field estimates of net trophic transfer of PCBs from prey fishes to Lake Michigan salmonids. *Environ. Sci. Technol.* 30(6): 1861-1865.

Jeremiason, J. D., K. C. Hornbuckle and S. J. Eisenreich (1994). PCBs in Lake Superior, 1978-1992: decreases in water concentrations reflect loss by volatilization. *Environ. Sci. Technol.* 28(5): 903-914.

Mac, M. J. and C. C. Edsal (1991). Environmental contaminants and the reproductive success of lake trout in the Great Lakes. *J. Tox. Environ. Health.* 33: 375-394.

Mac, M. J., T. R. Schwartz, C. C. Edsall and A. M. Frank (1993). Polychlorinated biphenyls in Great Lakes lake trout and their eggs: relations to survival and congener composition 1979-1988. *J. Great Lakes Res.* 19(4): 752-765.

Madenjian, C. P., T. J. DeSorcie, R. M. Stedman, E. H. J. Brown, G. W. Eck, L. J. Schmidt, R. J. Hesselberg, S. M. Chernyak and D. R. Passino-Reader (1999). Spatial patterns in PCB concentrations of Lake Michigan lake trout. *J. Great Lakes Res.* 25(1): 149-159.

Madenjian, C. P., R. J. Hesselberg, T. J. Desorcie, L. J. Schmidt, R. M. Stedman, L. J. Begnoche and D. R. Passino-Reader (1998). Estimate of net trophic transfer efficiency of PCBs to Lake Michigan lake trout from their prey. *Environ. Sci. Technol.* 32(7): 886-891.

Manchester-Neesvig, J.B., Valters, K. and Sonzogni, W.C., 2001. Comparison of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in Lake Michigan salmonids. *Environ. Sci. Technol.* 35(6), 1072-1077.

Marvin, C.H., et al., 2002. Surficial sediment contamination in lakes Erie and Ontario: a comparative analysis. *J. Great Lakes Res.* 28(3), 437-450.

Pearson, R. F., K. C. Hornbuckle, S. J. Eisenreich and D. L. Swackhamer (1996). PCBs in Lake Michigan water revisited. *Environ. Sci. Technol.* 30(5): 1429-1436.

Rodgers, P. W. and W. R. Swain (1983). Analysis of polychlorinated biphenyl (PCB) loading trends in Lake Michigan. *J. Great Lakes Res.* 9: 548-558.

Safe, S. H. (1994). Polychlorinated biphenyls (PCBs): environmental impact, biochemical and toxic responses, and implications for risk. *CRC Crit.Rev.Toxicol.* 24(2): 87-149.

Schmidt, L. J., and Hesselberg, R. J. (1992). A mass spectroscopic method for analysis of AHH-inducing and other polychlorinated biphenyl congeners and selected pesticides in fish. *Arch. Environ. Contam. Toxicol.* 23: 37-44.

Skoglund, R. S., K. Stange and D. L. Swackhamer (1996). A kinetics model for predicting the accumulation of PCBs in phytoplankton. *Environ. Sci. Technol.* 30(7): 2113-2120.

Skoglund, R. S. and D. L. Swackhamer (1993). Processes affecting uptake and fate of HOCs by phytoplankton. Environmental Chemistry of Lakes and Reservoirs. L. A. Baker. Washington, D.C., American Chemical Society. **237:** 559-573.

Skoglund, R. S. and D. L. Swackhamer (1999). Evidence for the use of organic carbon as the sorbing matrix in the modeling of PCBs accumulation in phytoplankton. *Environ. Sci. Technol.* 33: 1516-1519.

Stow, C. A. (1995). Factors associated with PCB concentrations in Lake Michigan salmonids. *Environ. Sci. Technol.* 29(2): 522-527.

Stow, C. A., S. R. Carp and J. F. Amrheim (1994). PCB concentration trends in Lake Michigan coho (Oncorhynchus kisutch) and chinook salmon (O. tshawytscha). *Can. J. Fish.Aq. Sci.* 51: 1384-1390.

Stow, C. A. and S. R. Carpenter (1994). PCB accumulation in Lake Michigan coho and chinook salmon: individual-based models using allometric relationships. *Environ. Sci. Technol.* 28: 1543-1549.

Stow, C. A., S. R. Carpenter, L. A. Eby, J. F. Amrhein and R. J. Hesselberg (1995). Evidence that PCBs are approaching stable concentrations in Lake Michigan fishes. *Ecol. Appl.* 5: 248-260.

Stow, C. A. and S. S. Qian (1998). A size-based probabilistic assessment of PCB exposure from Lake Michigan fish consumption. *Environ. Sci. Technol.* 32: 2325-2330.

Stow, C.A., Lamon, E.C., Qian, S.S. and Schrank, C.S., 2003. Will Lake Michigan lake trout meet the Great Lakes Strategy 2002 PCB reduction goal? *Environmental Science & Technology* 38, 359-363.

Swackhamer, D., J. Charles and R. Hites (1987). Quantitation of toxaphene in environmental samples using negative ion chemical ionization mass spectrometry. *Anal. Chem.* 59: 913-917.

Swackhamer, D. L. (1996). Studies of polychlorinated biphenyls in the Great Lakes. *Issues Environ. Sci.Technol.* 6: 137-153.

Swackhamer, D. L. and S. J. Eisenreich (1991). Processing of Organic Contaminants in Lakes. Organic Contaminants in the Environment: Sources, Environmental Pathways and Effects. K. C. Jones, Elsevier Applied Sciences**:** 33-86.

Swackhamer, D. L. and R. A. Hites (1988). Occurrence and bioaccumulation of organochlorine compounds in fishes from Siskiwit Lake. *Environ. Sci. Technol.* 22: 543-548.

Swackhamer, D. L. and R. S. Skoglund (1991). The role of phytoplankton in the partitioning of hydrophobic organic contaminants in water. Organic Substances and Sediments in Water. R. A. Baker. Chelsea, MI, Lewis Publishers. **2:** 91-105.

Swackhamer, D. L. and R. S. Skoglund (1993). Bioaccumulation of PCBs by phytoplankton: kinetics vs. equilibrium. *Environ. Toxicol. Chem.* 12: 831-838.

Swackhamer, D. L. and A. Trowbridge (1997). LMMBS Methods Compendium: Vol. 2 Organics and Mercury Sample Analysis Techniques, Chapter 1, Section 042. USEPA.

Swackhamer, D.L., Pearson, R.F. and Schottler, S., 1999. Air-water exchange and mass balance of toxaphene in the Great Lakes. *Environ. Sci. Technol.* 33, 3864-3872.

Swackhamer, D.L., Schottler, S. and Pearson, R.F., 1998. Toxaphene in the Great Lakes. *Chemosphere* 37, 2545-2561.

Thomann, R.V. and Connolly, J.P., 1984. Model of PCB in the Lake Michigan lake trout food chain. *Environ. Sci. Technol.* 18(65-72).

Thomann, R.V., Connolly, J.P. and Parkerton, T.F., 1992. An equilibrium model of organic chemical accumulation in aquatic food webs with sediment interaction. *Environ. Toxicol. Chem.* 11, 615-629.

Trowbridge, A. G. and D. L. Swackhamer (1999). Biomagnification of Toxic PCB Congeners in the Lake Michigan Foodweb. Persistent Bioaccumulative Toxic Compounds in the Environment. R. Lipnick, D. Muir, J. Hermens and K. C. Jones. Washington, DC, ACS Symposium Series Monograph**:** in review.